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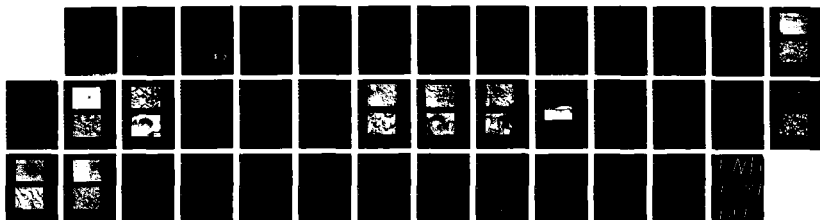
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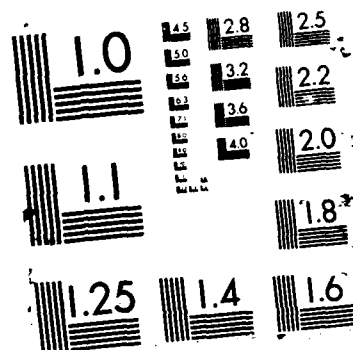
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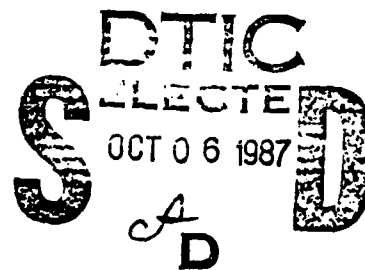
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Annual Report
Chemistry-Structure Interrelationships
for Calcareous Deposits
as Stand Alone Coatings

Contract N00014-86-K-0144

FLORIDA ATLANTIC UNIVERSITY
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Annual Report
Chemistry-Structure Interrelationships
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Introduction

For the past year the formation of calcareous deposits on metal surfaces under cathodic polarization has been investigated. Test procedures and cells have been developed for this work and a temperature control system has been designed and built which allows pertinent temperatures to be obtained for experiments. The potentiostatic current decay on several substrates with various surface finishes has been determined. Potentiostatic versus galvanostatic testing has been contrasted. New methods of quantifying both the electrical and physical properties of the films are currently being developed.

Temperature Control System

In order to investigate the effects of temperature on the formation of calcareous deposits efficiently and in a timely manner a new system of temperature control needed to be developed beyond that previously existing at the laboratory. Since each experiment can require upwards of 7000 minutes, it is important to have the capability of running parallel experiments. To accomplish this goal the constant temperature system must operate at several different temperatures. In order to keep costs down and to maintain maximum flexibility of the temperature system a distributed system consisting of a single large cooling unit supplying coolant to three constant temperature units was designed and built (Fig. 1). This allows three different temperatures to be run concurrently with the option of

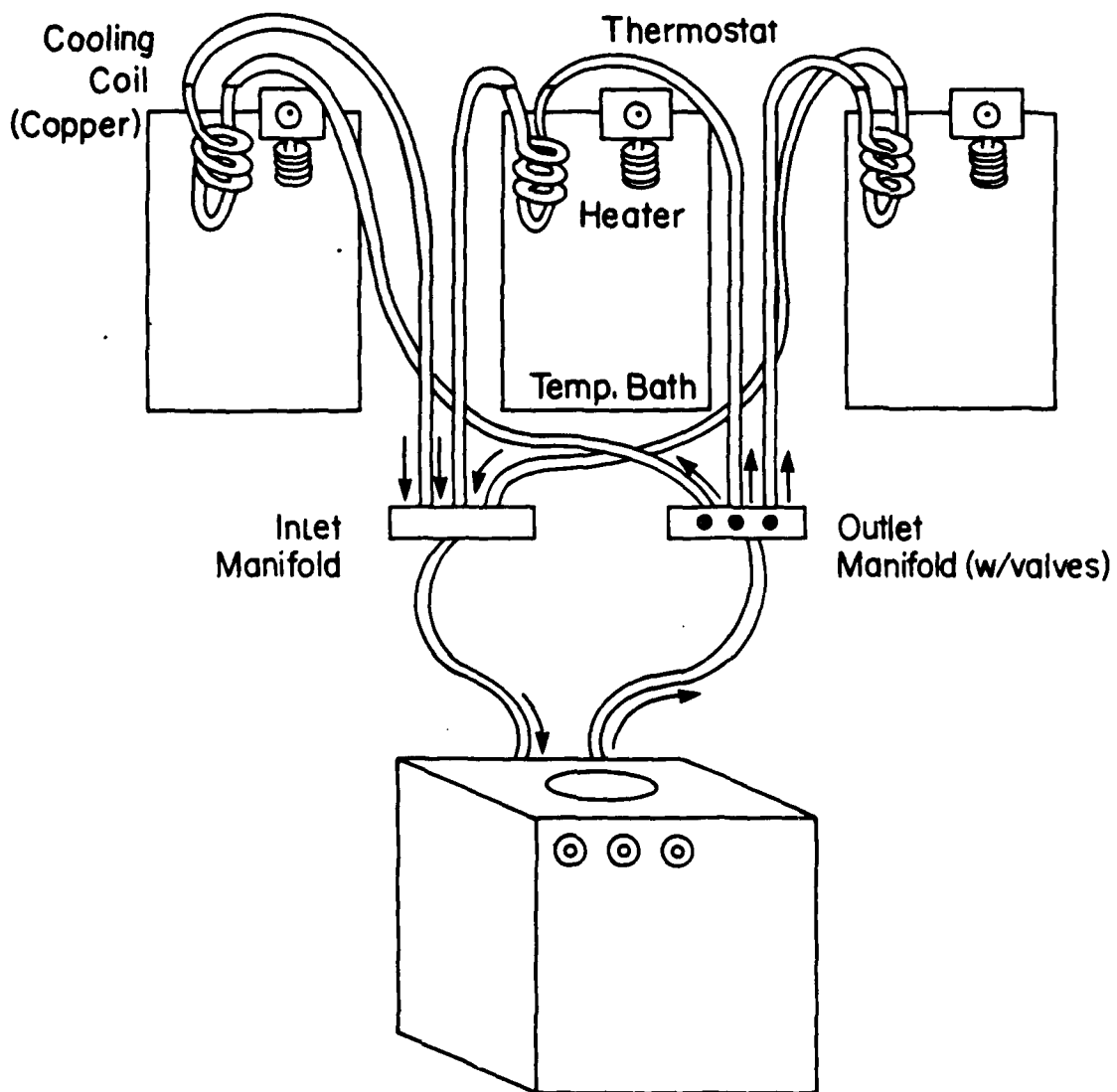


Figure 1 Recirc. Cooler.

adding additional constant temperature units at a later date at a substantially lower cost than three units with separate coolers.

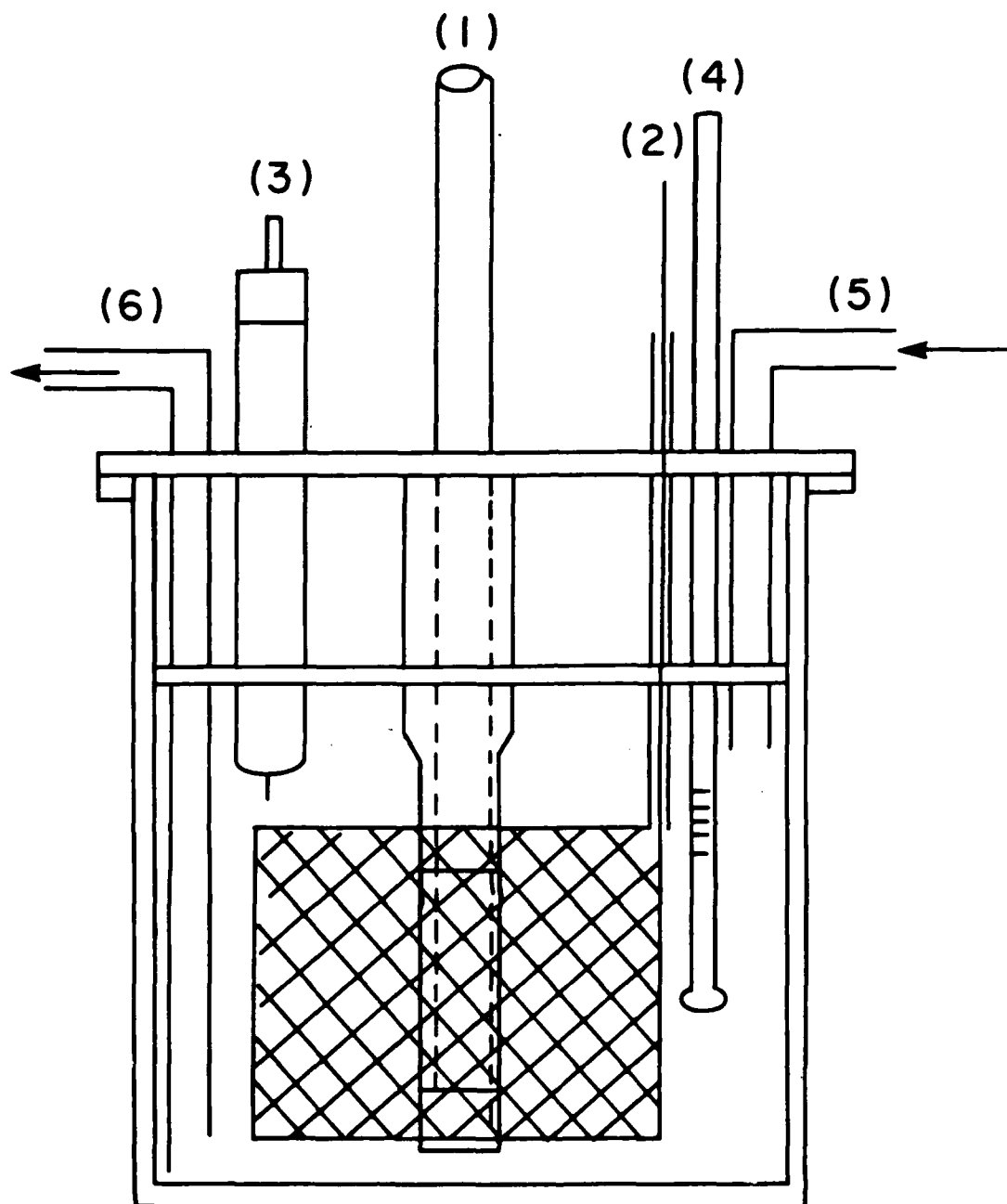
Test Cells

A test cell design developed for a previous project supported by Sea Grant¹ was updated and revised to utilize less expensive off-the-shelf components (Fig. 2). Eight of these cells were constructed for this project. These utilize a cylindrical electrode one inch in length by one half inch diameter. These are mounted on a stainless steel shaft between Delrin spacers (Fig. 3). A platinized niobium mesh counter electrode encircles the steel specimen. Cell potential is monitored via a saturated calomel reference electrode. All experiments utilized fresh flowing seawater as the electrolyte.

Galvanostatic vs. Potentiostatic Testing

Potentiostatic Control

Several potentiostatically controlled polarization experiments were performed using potentials of -800 mV, -900 mV, and -1000 mVSCE. Figure 4 shows the current density as a function of exposure time for various cathodic potentials. As expected all samples showed decreasing current density with time. Experiments conducted at -800 and -900 mVSCE showed a rapid drop in current in the first few hours reaching a steady state current; however, the -1000 mVSCE samples showed a lower rate of current decrease continuing over the entire period of the test. In contrast an



- | | |
|-------------------------|---------------------|
| 1). Specimen Holder | 4). Thermometer |
| 2). Counter Electrode | 5). Solution Inlet |
| 3). Reference Electrode | 6). Solution Outlet |

Figure 2 Electrochemical Cell.

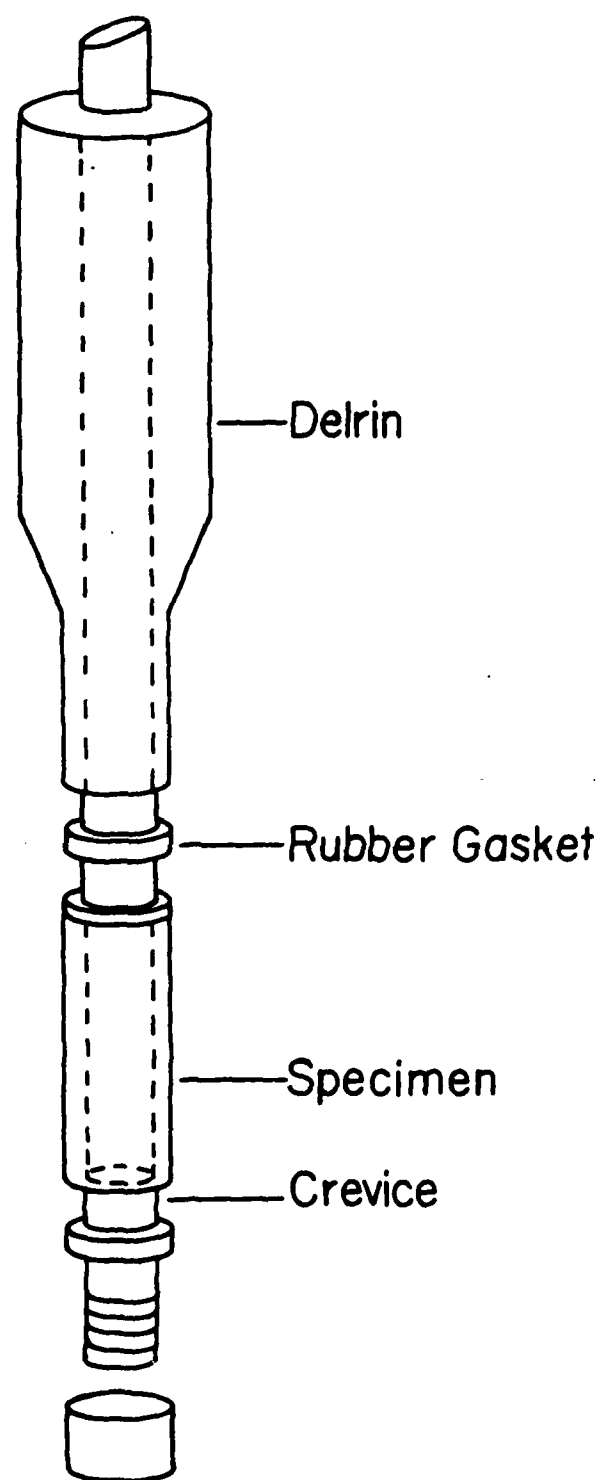


Figure 3 Specimen Holder.

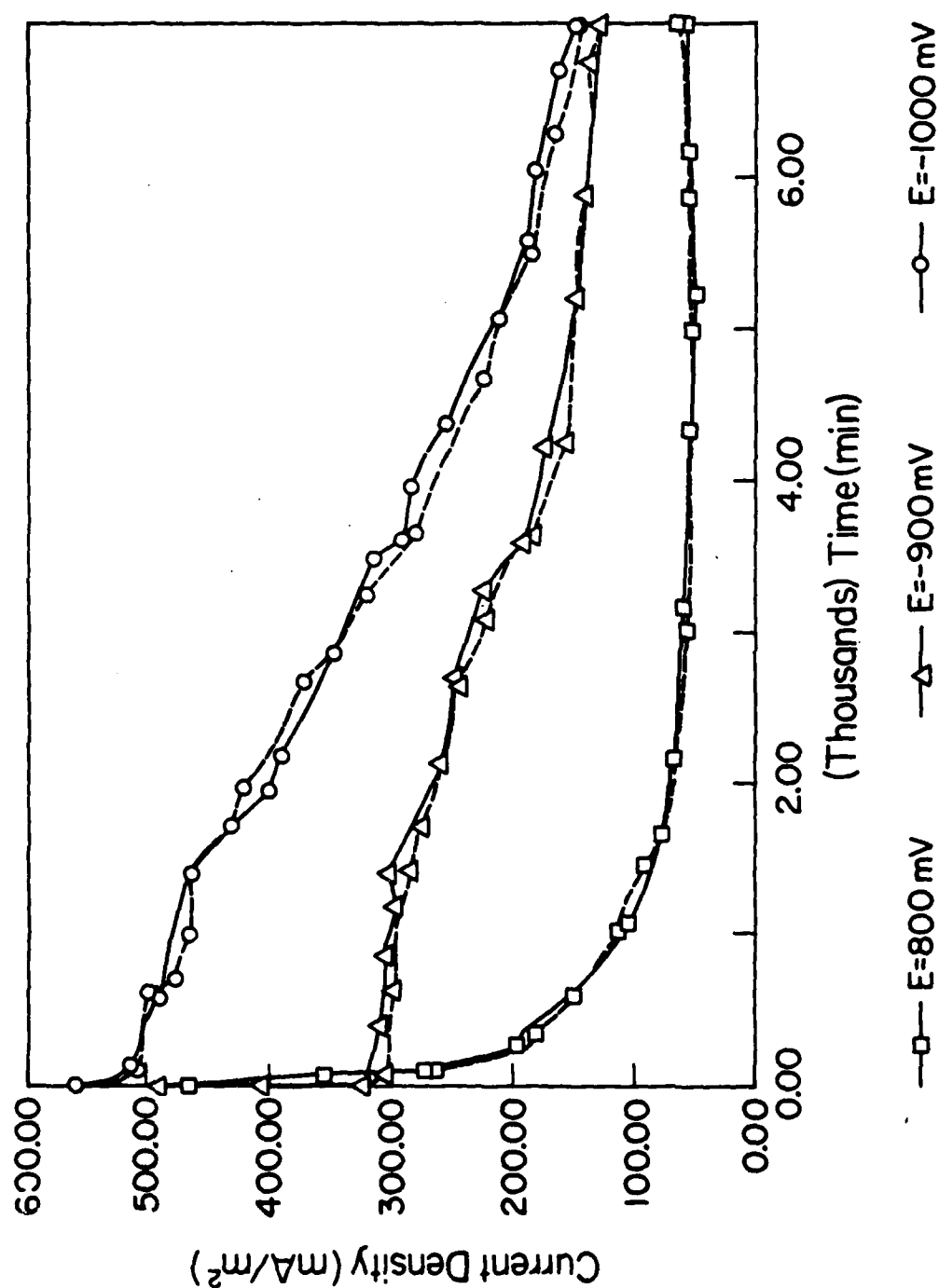


Figure 4 Current Density vs. Time
Potentiostatic mode
T=25°C, flow rate=40 ml/min

artificial solution containing Na^+ , Cl^- , SO_4^{2-} , and HCO_3^- in the concentrations of natural seawater, but containing no Mg^{+2} or Ca^+ showed no significant decrease in current density with time (Fig 5). This is in agreement with previous work² in indicating a precipitated calcium and magnesium salt film caused the decrease in cathodic current density.

All of the specimens were examined visually. None of the specimens held at -900 mVSCE showed any sign of corrosion even after 7000 minutes of exposure, thus this potential provides complete protection. These specimens were covered with a uniform greyish-white film. At -800 mVSCE specimens showed a brownish discoloration apparently due to surface rusting indicating incomplete protection under the test conditions (25°C, inlet flow of 40 ml/min). It is, however, interesting to note this discoloration was not observed after 4000 minutes. A greyish/white base film similar to that found at -900 mV formed at -1000 mVSCE, however, it was covered by clusters of milky white material. These clusters were interpreted as manifestations of hydrogen evolution.

When observed under the Scanning Electron Microscope distinct differences could be observed in the morphology of films formed at the different potentials. Specimens polarized at -800 mVSCE showed a loose film of flower like structures (Fig. 6 and 7). Films formed at -900 mVSCE consisted of a dense, fine scale made of small fibrils (Fig.

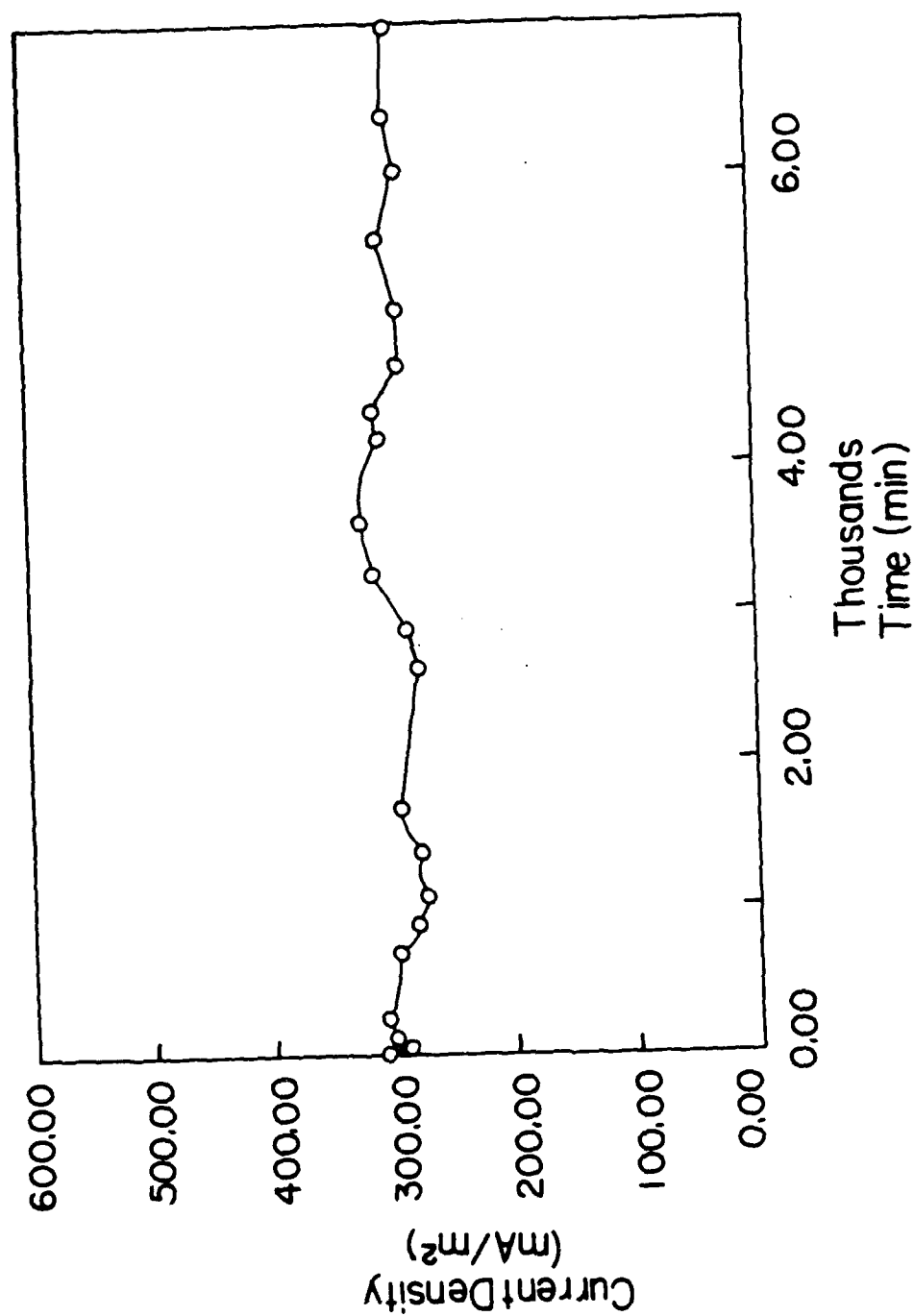


Figure 5 Current Density versus Exposure Time
at -900 mV Potentiostatic Polarization in
Synthetic Sea Water.

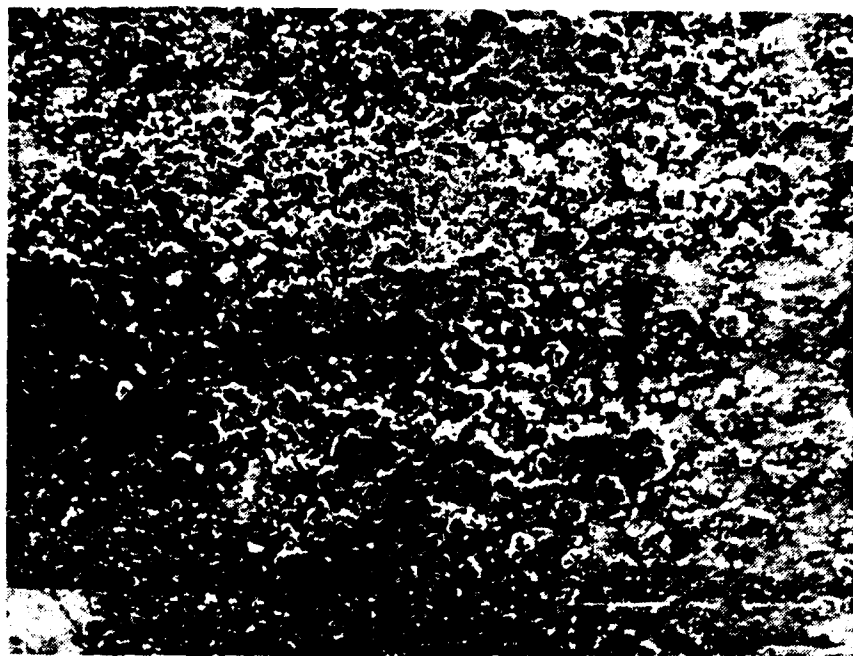


Figure 6. Scanning electron micrograph of calcareous deposit formed under -800 mV polarization at a magnification of 120 X.

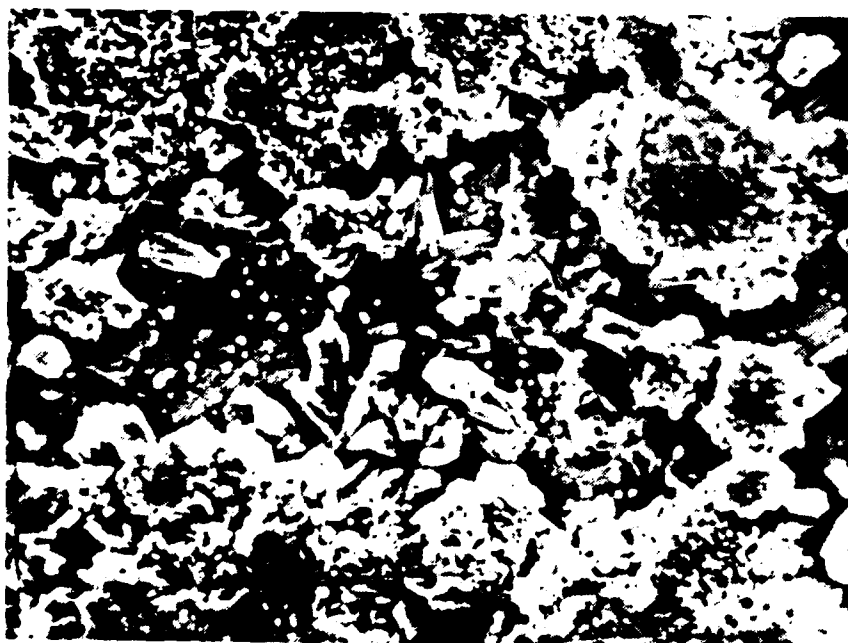


Figure 7. Scanning electron micrograph of calcareous deposit formed under -800 mV polarization at a magnification of 600 X.

8 and 9). At -1000 mVSCE the film is composed of larger globules (Fig. 10 and 11). This porosity is believed due to hydrogen evolution.

Specimens were also viewed edge-on for the purpose of determining the calcareous deposits thickness. Edge on SEM viewing revealed that deposit thickness varied circumferentially about the specimens. In view of this observation a mean value of ten selected positions on the sample's circumference were used as a measure of film thickness. This data was also compared to thicknesses measured with a micrometer. The following chart reports the results of mean deposit thickness determinations as a function of potential:

Potential (mV)	-800	-900	-1000
Film Thickness ($\times 10^4$ cm)	40.24	90.02	167.3

It can be noted that a more negative protection potential results in a thicker calcareous film. This trend would be expected since pH production should be a function of applied potential.

Galvanostatic Control

In reviewing the literature available on the cathodic protection of metals in seawater one is immediately struck with the paucity of data pertaining to galvanostatic polarization. This is probably due as much to the greater availability of potentiostats versus galvanostats and a desire to correlate results with those available in the literature as for any technical reason. In this project

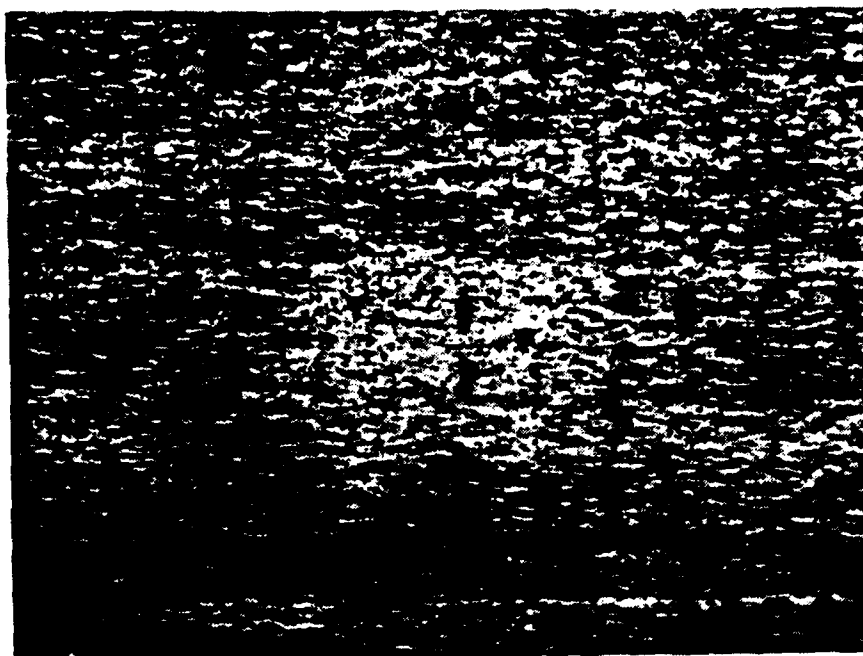


Figure 8. Scanning electron micrograph of calcareous deposit formed under -900 mV polarization at a magnification of 120 X.

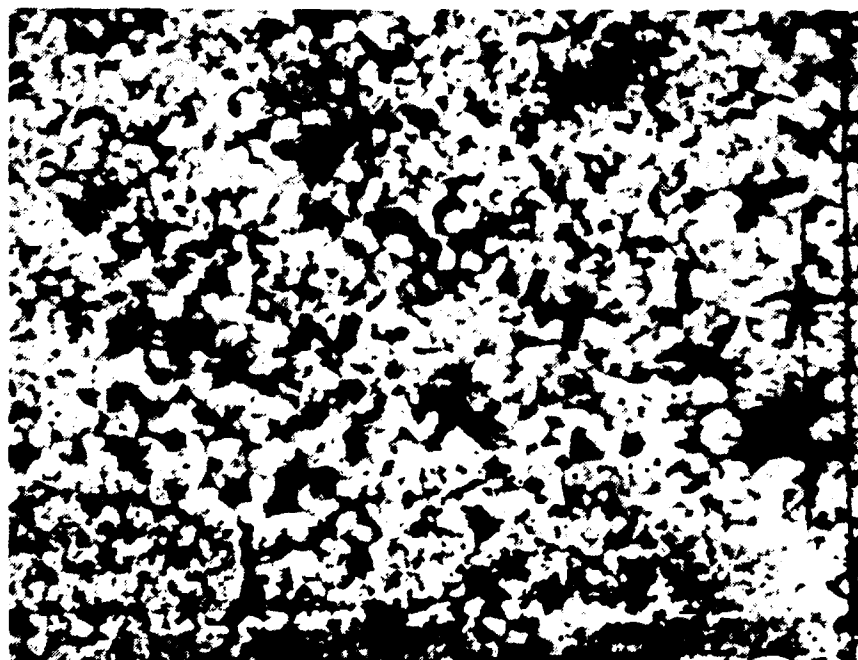


Figure 9. Scanning electron micrograph of calcareous deposit formed under -900 mV polarization at a magnification of 600 X.



Figure 10. Scanning electron micrograph of calcareous deposit formed under -1000 mV polarization at a magnification of 120 X.

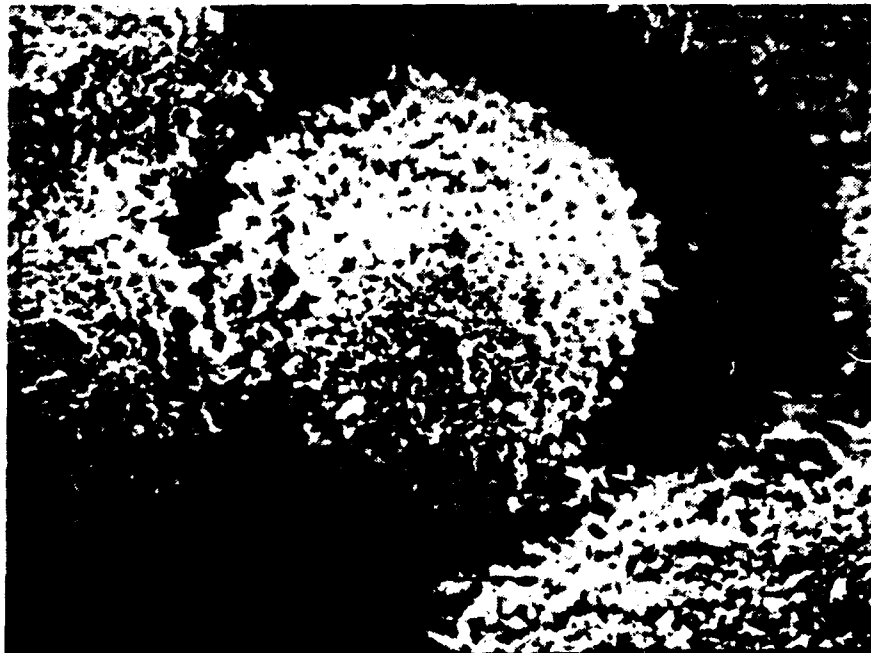
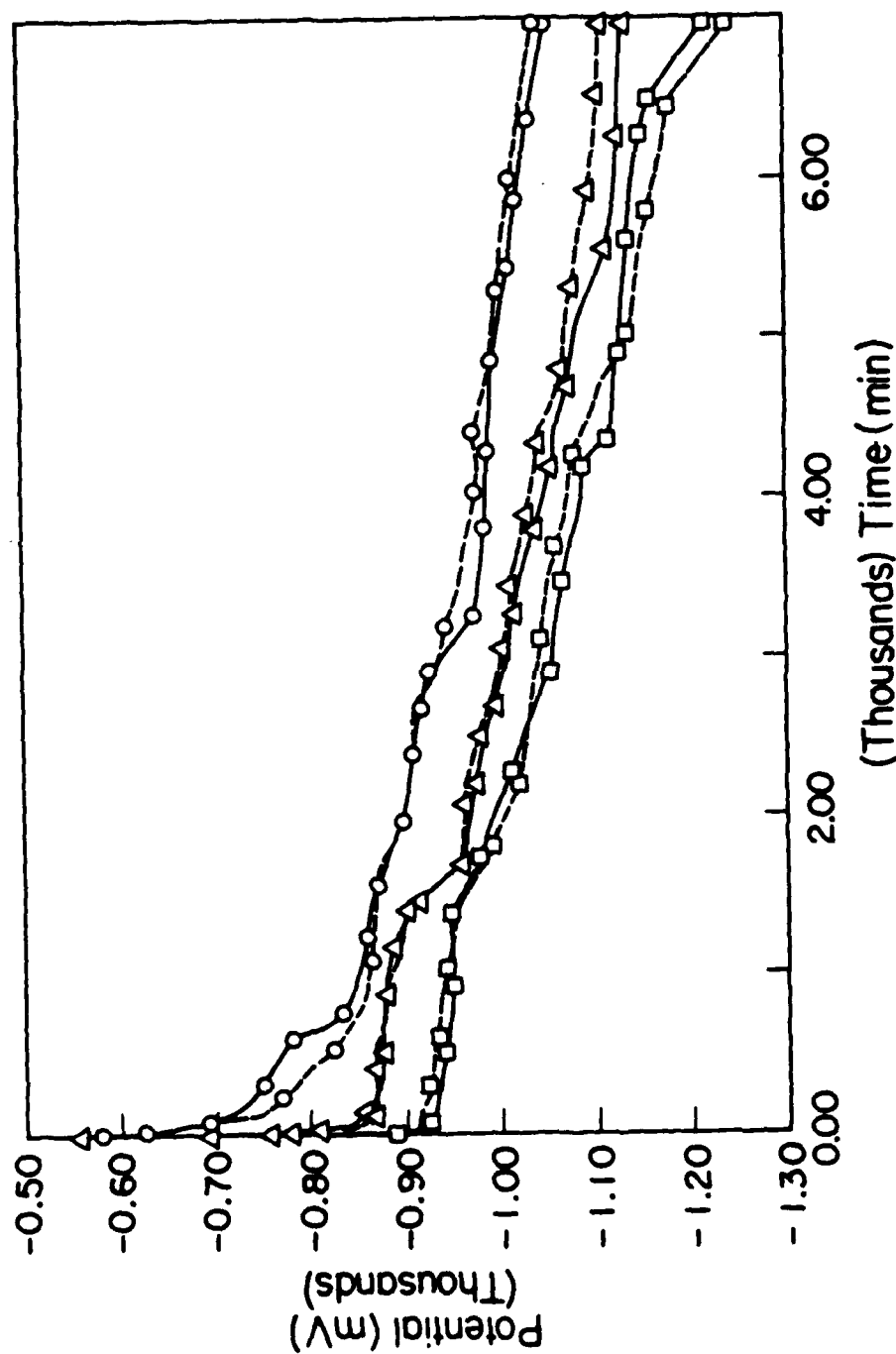


Figure 11. Scanning electron micrograph of calcareous deposit formed under -1000 mV polarization at a magnification of 600 X.

galvanostatic polarization is being investigated to determine if it has any advantages over potentiostatic polarization for the formation of protective calcareous films.

The results of galvanostatic tests plotting potential change versus time are shown in Figure 12. These tests were run at controlled currents of 0.25 (246.8 mA/m²), 0.30 (296.2 mA/m²), and 0.35 mA (345.5 mA/m²). In each case there was a rapid initial polarization, followed by a slower drop in potential. Higher applied currents resulted in more rapid initial polarizations, however, after the initial period of polarization the potential change with time was approximately the same at all applied currents. As one might expect larger applied currents yielded lower final potentials. In every case the potential dropped below -1000 mVSCE during the 7000 minute test.

Upon visual examination the specimens polarized at 0.25 mA were covered with a greenish white coating which changed rapidly to a brown color upon removal from the electrolyte, indicating that under polarization iron was precipitated as a Fe⁺² species, most likely a hydroxide or oxychloride, which upon exposure to air was oxidized to the Fe⁺³ state. At the higher applied currents of 0.30 and 0.35 mA a greyish white coating with clusters of milky white scale were observed. It is believed that this is an indication of significant hydrogen evolution.



—○— $i = 0.25 \text{ mA}$ —△— $i = 0.30 \text{ mA}$ —□— $i = 0.35 \text{ mA}$

Figure 12 Current Density vs. Time
Galvanostatic mode
 $T = 25^\circ \text{C}$, flow rate = 40 ml/min

Again the morphology of the scales was determined using the SEM. From these observations one can conclude that a higher current density results in a coarser, but thicker deposit. At 0.25 mA a fine grained film with a flower like structure was present (Fig. 13 and 14). This contrasts with a spherical type structure observed for the 0.30 mA case (Fig. 15 and 16). The scale formed at 0.35 mA showed a multi-layered structure. The surface layer is an amorphous structure made up of fine fibrils (Fig. 17 and 18). In some areas this layer appears to have broken away due to impingement during growth (Fig. 19). The porous nature of the structure is believed due to hydrogen evolution.

The mean deposit thickness data for galvanostatically controlled specimens after 7000 minutes of exposure is shown below:

Potential (mA/m ²)	246.8	296.2	345.5
Film Thickness (x10 ⁴ cm)	103.45	140.15	168.92

Again as expected the higher currents yielded the large film thicknesses, attributable to increased hydroxide production.

Combined Galvanostatic/Potentiostatic Control

From the previous data it can be noted that the steel surface polarized more quickly under galvanostatic control, however, it also rapidly entered the region of hydrogen evolution. Films formed more slowly under potentiostatic control, but hydrogen evolution did not appear to occur at potentials of -900 mVSCE or more. In order to try to take advantage of the best of both approaches it was decided to

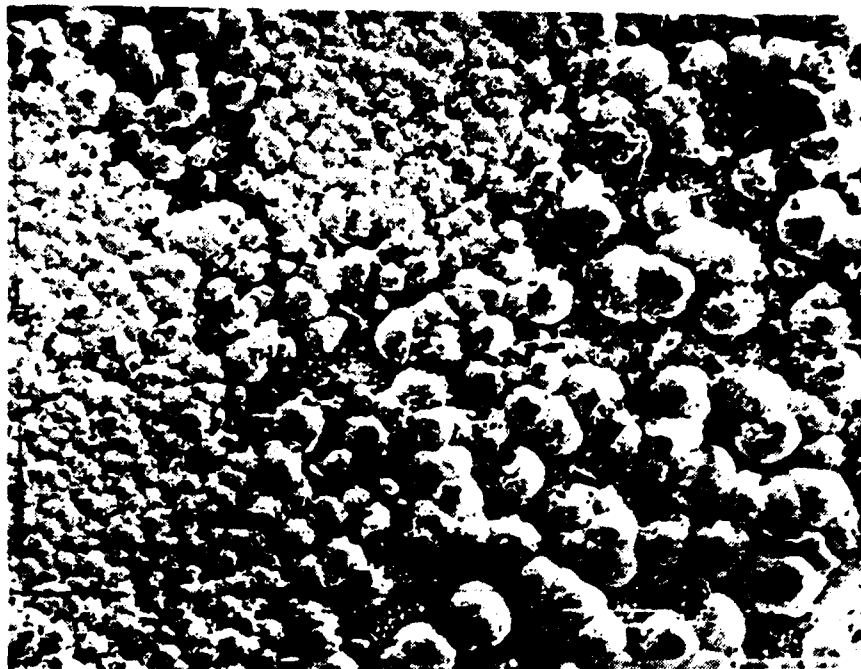


Figure 13. Scanning electron micrograph of calcareous deposit formed under 246.8 mA/m^2 polarization at a magnification of 120 X.

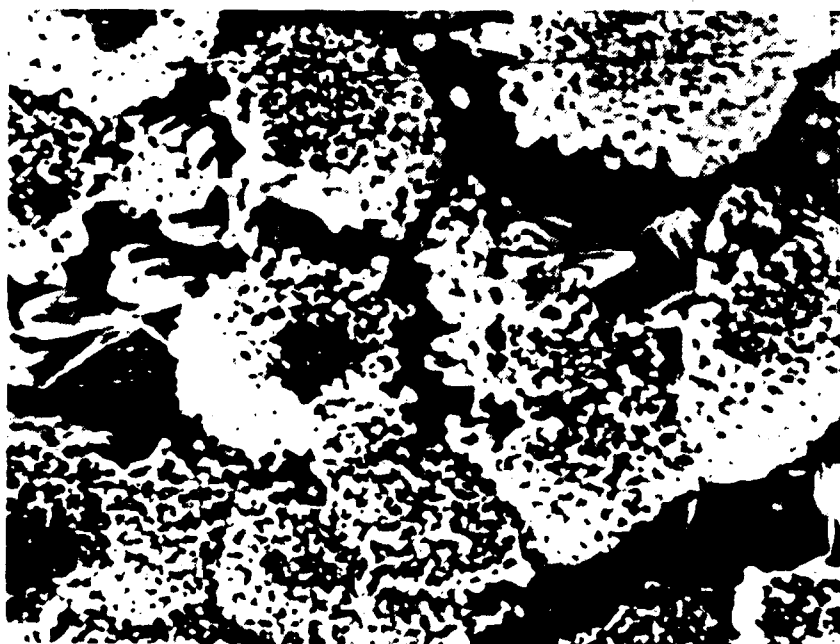


Figure 14. Scanning electron micrograph of calcareous deposit formed under 246.8 mA/m^2 polarization at a magnification of 600 X.



Figure 15. Scanning electron micrograph of calcareous deposit formed under 296.2 mA/m^2 polarization at a magnification of 120 X.

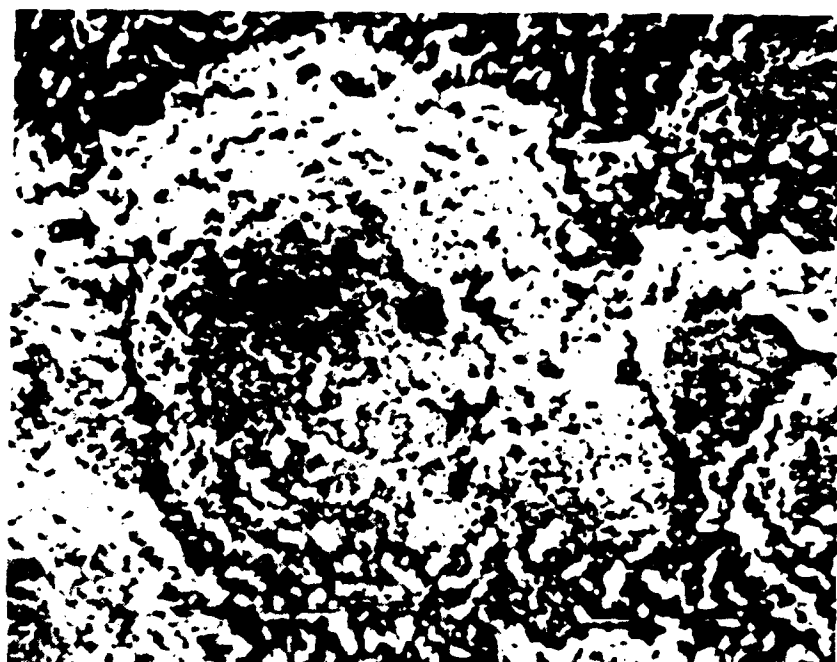


Figure 16. Scanning electron micrograph of calcareous deposit formed under 296.2 mA/m^2 polarization at a magnification of 600 X.

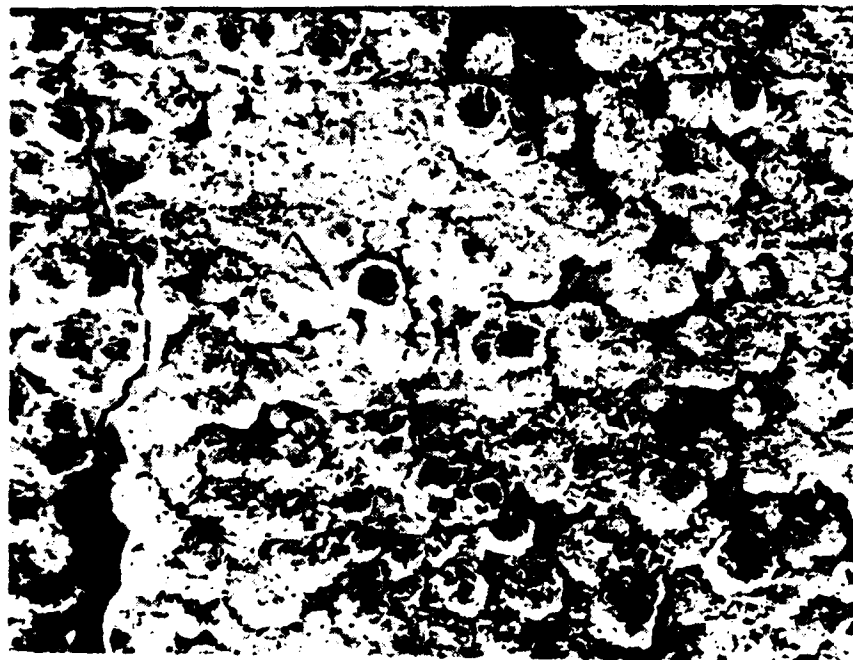


Figure 17. Scanning electron micrograph of calcareous deposit formed under 345.5 mA/m^2 polarization at a magnification of 120 X.



Figure 18. Scanning electron micrograph of calcareous deposit formed under 345.5 mA/m^2 polarization at a magnification of 600 X.

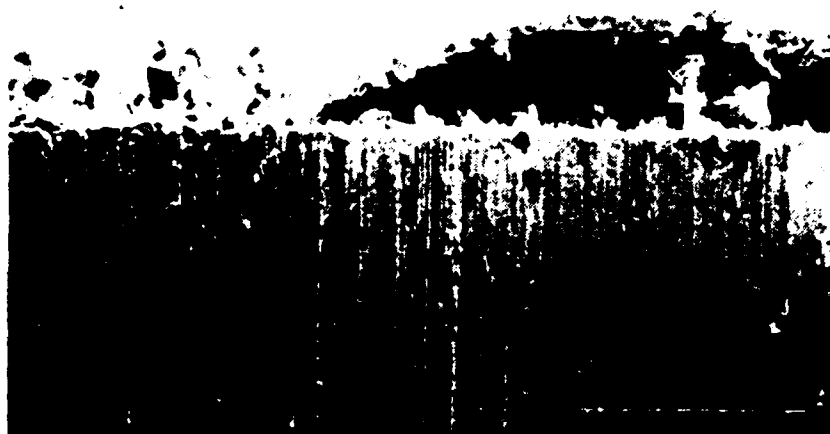


Figure 19. Scanning electron micrograph of calcareous deposit delaminated from substrate at a magnification of 200 X.

try a combined galvanostatic/potentiostatic control, that is the specimen was held under galvanostatic control until it reached -900 mVSCE and the control was switched to potentiostatic so that hydrogen evolution potentials were not reached. Initial galvanostatic currents of 0.25 mA, 0.30 mA, and 0.35 mA were selected since baseline data existed for these currents.

At an initial current density of 0.25 mA it required approximately 2000 minutes for the potential to drop to -900 mVSCE (Fig. 20). The required potentiostatic current then drops comparatively slowly. For an initial current density of 0.30 mA it took about 1400 minutes to reach -900 mVSCE (Fig. 20). The 0.35 mA case took only 4 minutes to reach -900 mVSCE (Fig. 20). By comparing Figure 20 to Figure 4 it can be seen that after 7000 minutes the potentiostatic specimen required about 125 mA while the combined mode require less, about 70 mA and 60 mA for specimens initially held at 0.30 mA and 0.35 mA respectively. The sudden drop in current upon switching from galvanostatic to potentiostatic mode is interesting if not disturbing and will be the subject of further study.

Visually the combined mode specimens were covered with a greyish/white film similar in appearance to that on the -900 mVSCE potentiostatic specimens. They showed no rust indicating incomplete protection or milky white deposits associated with hydrogen evolution.

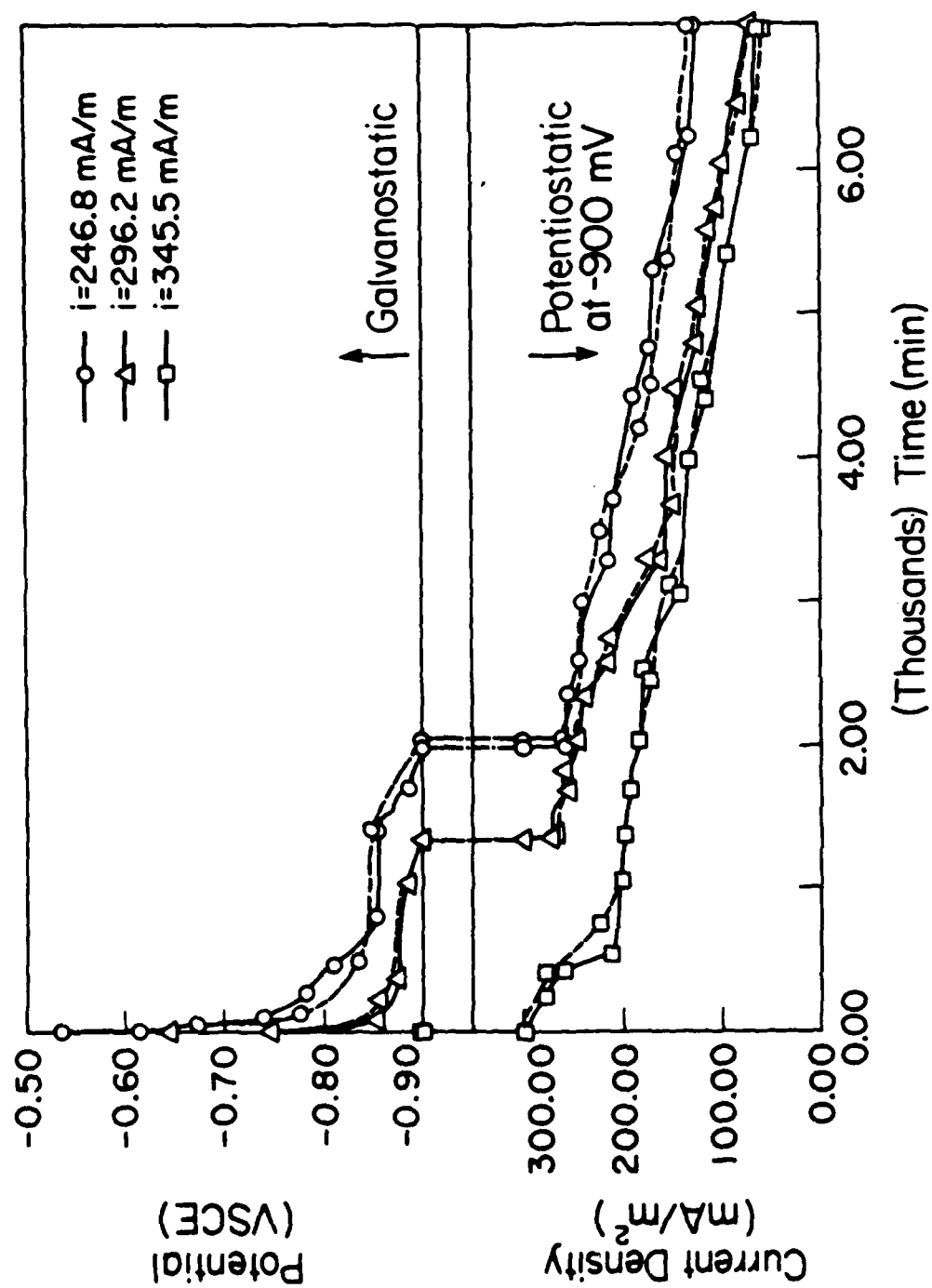


Figure 20 Current Density vs. Time
Galvanostatic mode
 $T = 25^\circ\text{C}$, flow rate = 40 ml/min

Under the electron microscope the films formed with a 0.25 and 0.30 mA pretreatment showed a dense flower like structure (Fig. 21-24). A less dense flower like structure was observed for the -800 mVSCE potentiostatic specimens. However, the 0.35 mA pretreatment resulted in a film showing a fibril type structure (Fig. 25 and 26). This is more in line with the deposits formed at -900 mVSCE (Fig. 8 and 9).

The final film thickness as a function of galvanostatic pretreatment for -900 mV is shown below:

Initial current (mA/m ²)	246.8	296.2	345.5
Film Thickness (x10 ⁴ cm)	103.45	140.15	168.92

Note that as previously presented the film thickness for a potentiostatically controlled specimen at -900 mVSCE is about 83×10^{-4} cm. Therefore, the galvanostatic pretreatment resulted in a significantly thicker film, especially at 0.30 and 0.35 mA.

Substrate

A series of experiments have been undertaken to investigate the effects of substrate on the formation of calcareous deposits. Several alloys were investigated each with several surface finishes. The initial metals were A-710 grade 3 class 2, HY-80, A-536 direct quenched, and high purity iron (zone refined 99.999%). The initial surface finishes were no. 600 grit and no. 1100 grit sandpaper. Mineral spirits were used as a lubricant during the polishing process. Specimens were cleaned with acetone before exposure. Based on the galvanostatic/potentiostatic

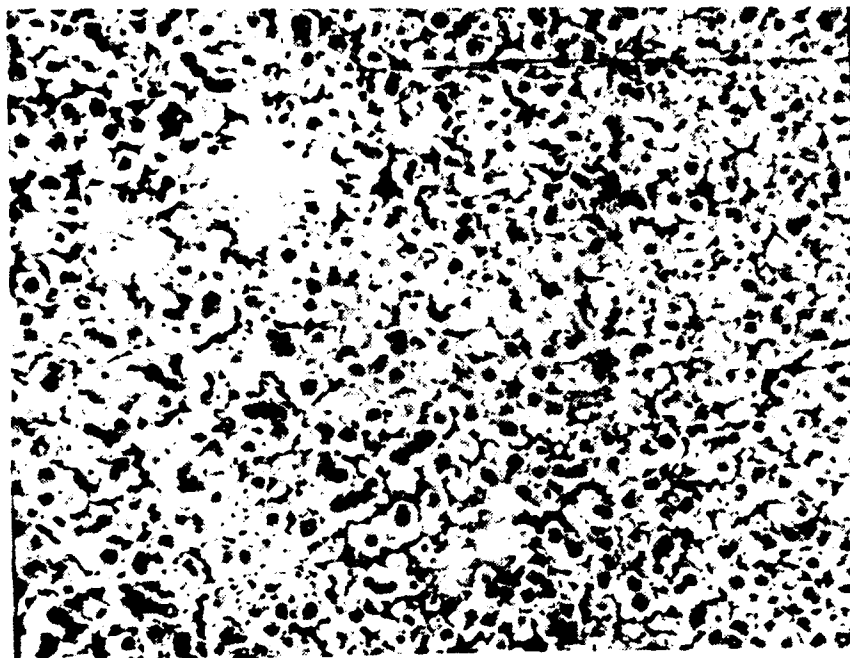


Figure 21. Scanning electron micrograph of calcareous deposit formed under 246.8 mA/m^2 & -900 mV polarization at a magnification of 120 X.

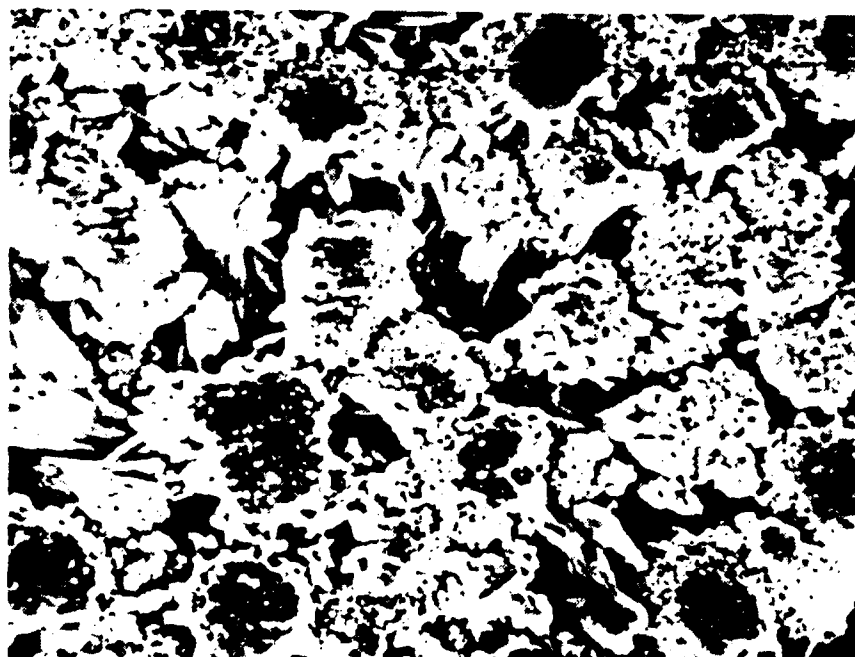


Figure 22. Scanning electron micrograph of calcareous deposit formed under 246.8 mA/m^2 & -900 mV polarization at a magnification of 600 X.

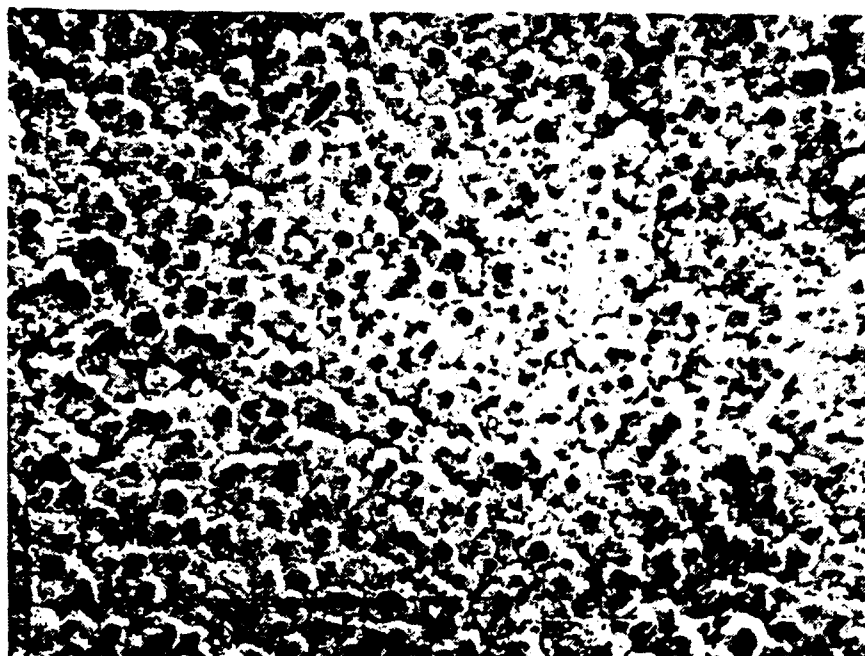


Figure 23. Scanning electron micrograph of calcareous deposit formed under 296.2 mA/m^2 & -900 mV polarization at a magnification of 120 X.



Figure 24. Scanning electron micrograph of calcareous deposit formed under 296.2 mA/m^2 & -900 mV polarization at a magnification of 600 X.

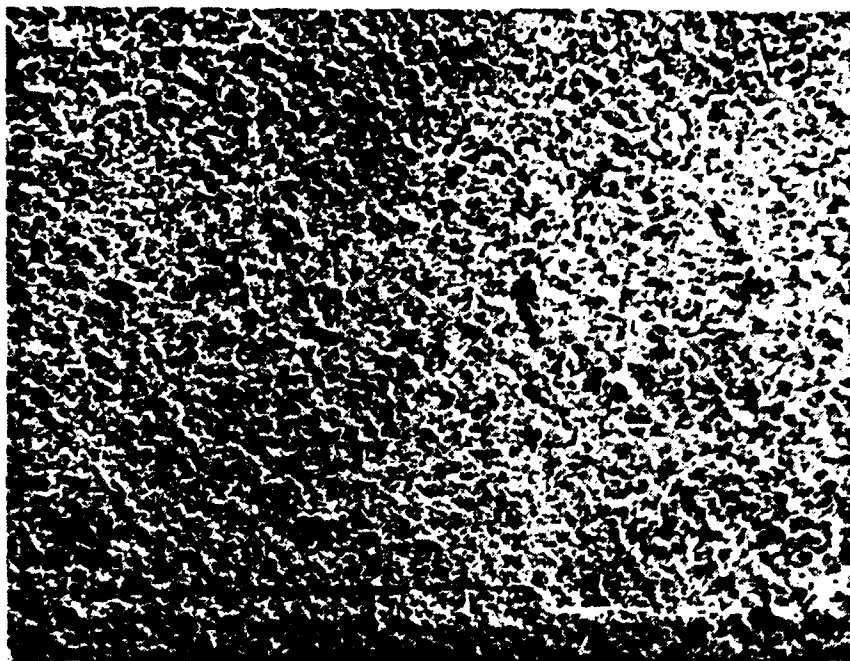


Figure 25. Scanning electron micrograph of calcareous deposit formed under 345.5 mA/m^2 & -900 mV polarization at a magnification of 120 X.

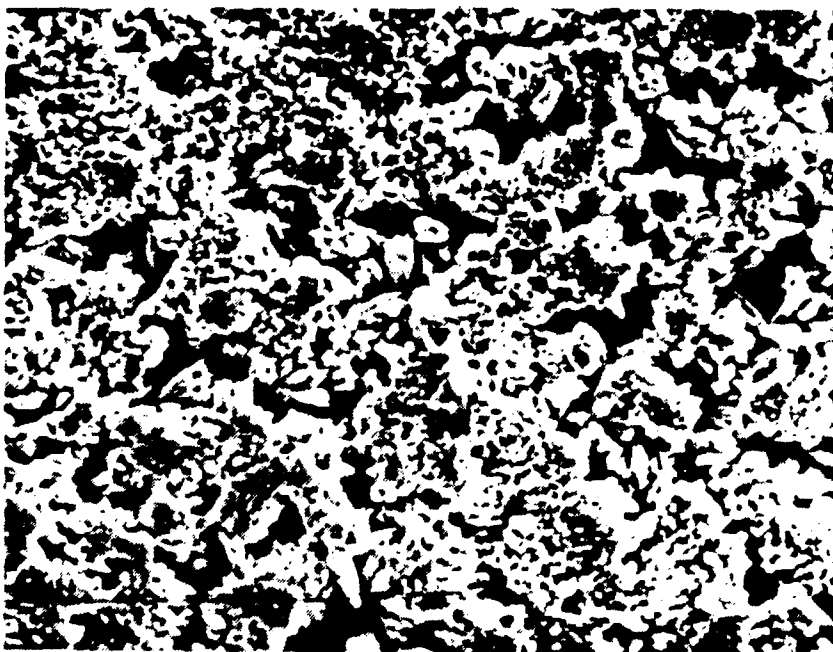


Figure 26. Scanning electron micrograph of calcareous deposit formed under 345.5 mA/m^2 & -900 mV polarization at a magnification of 600 X.

data showing no significant advantage to a galvanostatic test these tests were run potentiostatically under the following conditions; -900 mVSCE, 25°C, 100ml/min flow.

These data have revealed some trends. The time of formation of the calcareous deposit and the resulting current density decrease was markedly and consistently less for the 600 finish than for the 1100 finish. The time of formation of a film causing significant polarization was between 300 and 600 minutes for the 600 finish and between 1200 and 1800 hours for the 1100 finish (Fig. 27).

Observations under the electron microscope revealed that the uniform protective films consisted of small densely packed crystals and the less protective films were made up of large globular sparsely packed crystals.

The direct quenched A-536 was an exception to this trend. This steel formed little or no protective film. This was confirmed both visually, showing a sparse to nonexistent film even after 100 hrs, and electrochemically, showing little current decay during the duration of the experiment (Fig. 28).

Possible explanations for the observed differences include local pH variations due to differences in actual exposed surface area and localized current density differences due local surface geometry, composition, or structure. The observed structures could then be explained in terms of the density of nucleation sites, fewer resulting

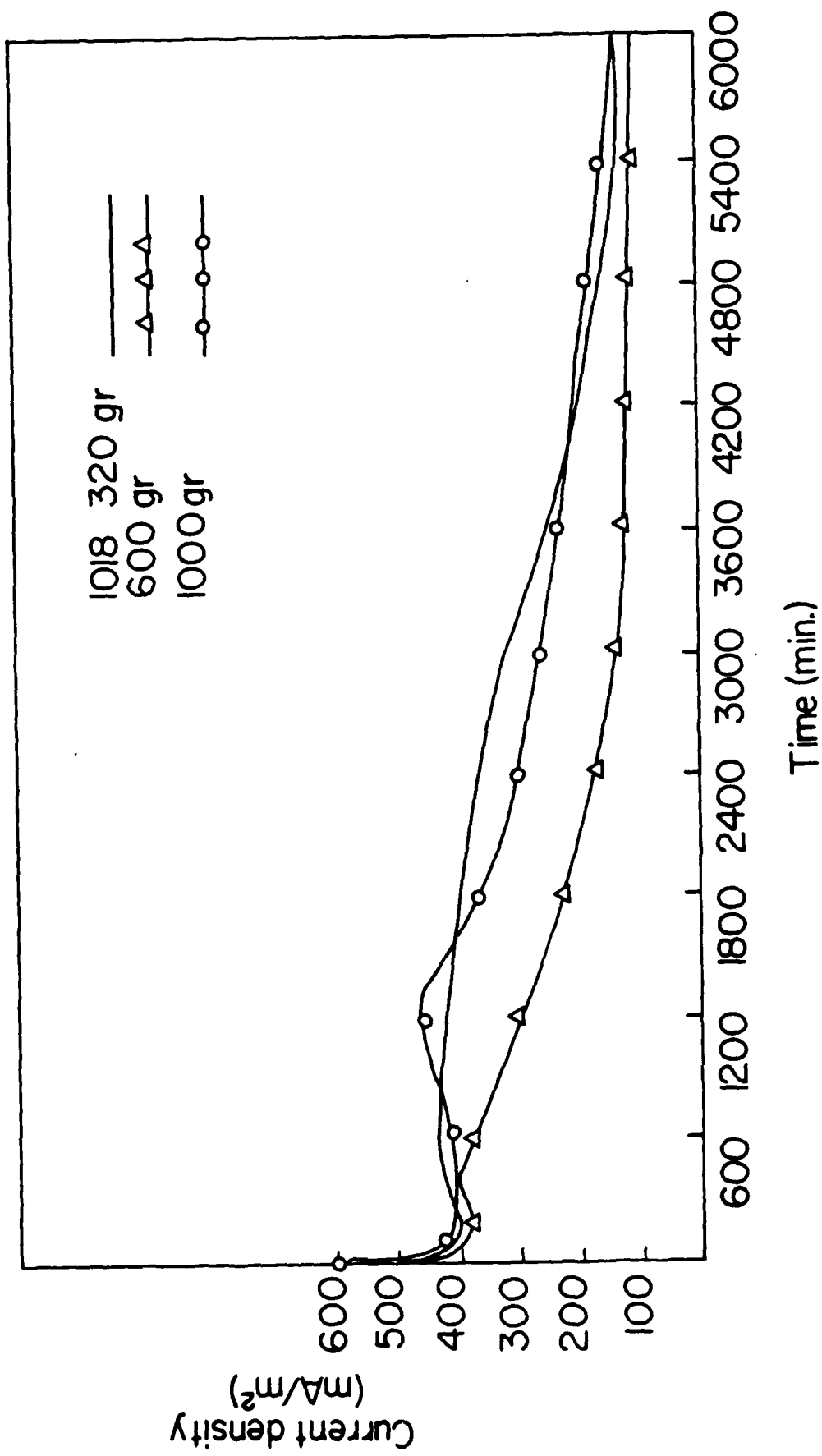


Figure 27 Current Density vs. Time for Various Surface Finishes.

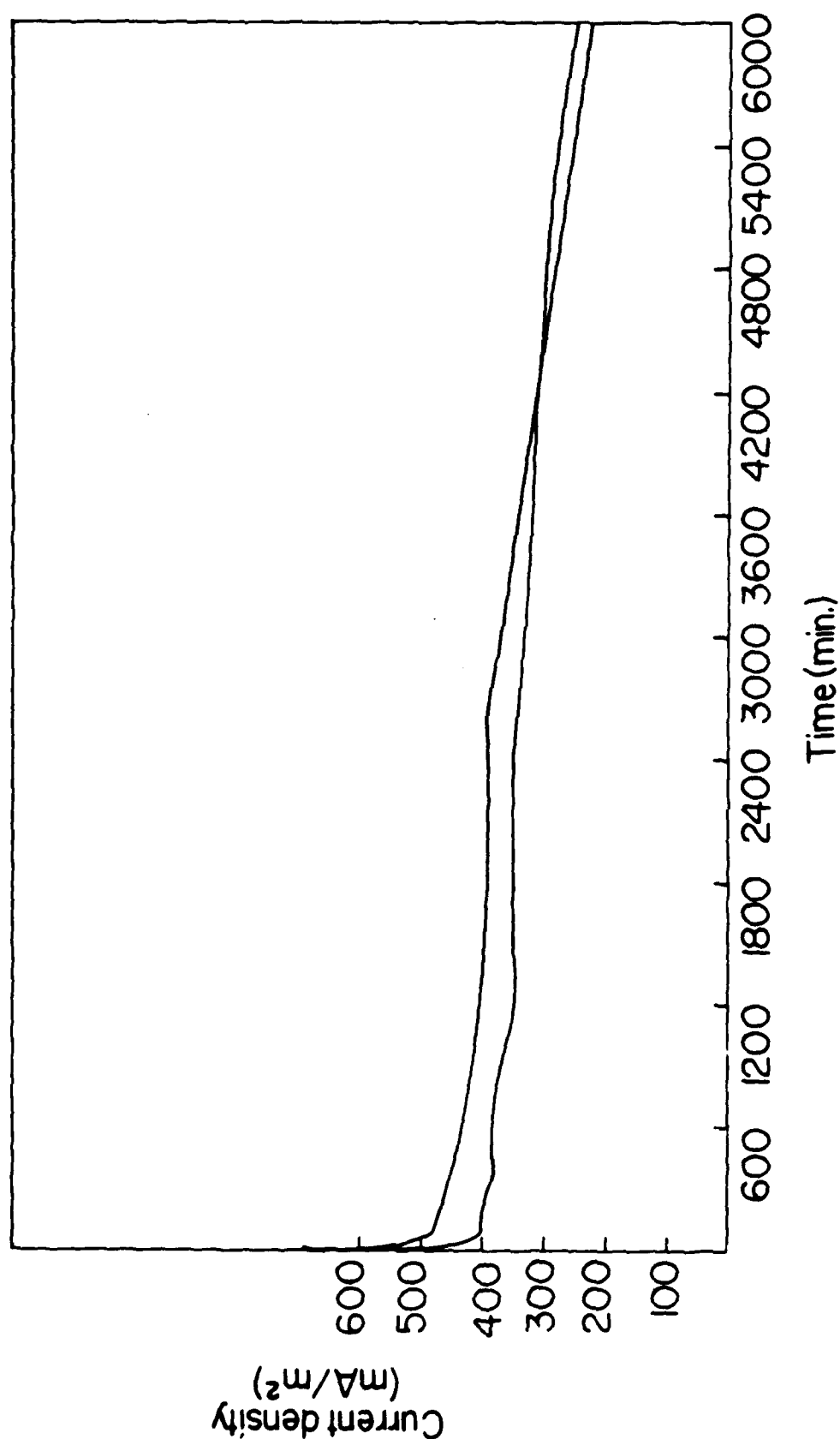


Figure 28 Current Density vs. Time A-537
grade 5, 600 gr Direct Quenched.

in large crystals and poor coverage and more in small crystals and uniform coverage.

Film Resistance

AC impedance was chosen as the most promising method to accurately determine the electrical properties of the deposited calcareous film. This method allows the magnitude of individual components of an electrical analogy to the film to be determined³. These components include solution, polarization (charge transfer), and film resistance. In addition to use in determining the electric analogy of the film, the impedance data can be used in the determination of the porosity of the film, via use of the Nyquist plot.

Other methods, such as the current interrupter and DC resistance only allow determination of the solution and the combination of the polarization and film resistance. However, it will be seen that a combination of AC impedance with one of these is necessary to extract the required information.

The experimental set up for AC impedance consisted of a Hewlett-Packard function generator, and Aardvark potentiostat, and an output recording device (an X-Y recorder or a Tektronix oscilloscope). While the Aardvark potentiostat is not optimum for AC impedance, it proved adequate for our initial work. A 10 mV sinusoidal signal was applied externally through the potentiostat and a plot of potential versus current was recorded in the form of a Lissajou figure. From this the real and the imaginary

impedance can be found. A plot of real versus imaginary impedances for the frequency range of 10 kHz to 1mHz was constructed (Nyquist plot). Typical data is shown in Figure 29.

From this figure it is apparent that as the low frequency range was reached, the semi-circle tailed away and lead to what may be a larger semi-circle. This larger semi-circle was interpreted as resulting from the electrical analogy being a parallel R-C circuit as in Figure 30. The high frequency data shows, as expected, the solution resistance was effectively zero. The polarization resistance was determined by extrapolating the first semi-circle to the real axis. This can be done with reasonable confidence. The difficulty was in determining the film resistance. In order to complete the second semi-circle data must be obtained from considerably below 1 mHz. Slow changes in the film properties during the test, which took a minimum of 3 hrs at 0.1 mHz (longer if a more sophisticated data analysis such as Fourier was used), result in the inability to produce reproducible measurements at less than 1 mHz.

In addition to the Nyquist plot, a Bode plot can be used to find the polarization resistance. In this case the log of the impedance (Z) is plotted against the log of the frequency (f). An example of this plot is shown in Figure 31. This method is not as accurate as the Nyquist plot, but is less sensitive to noise in the data.

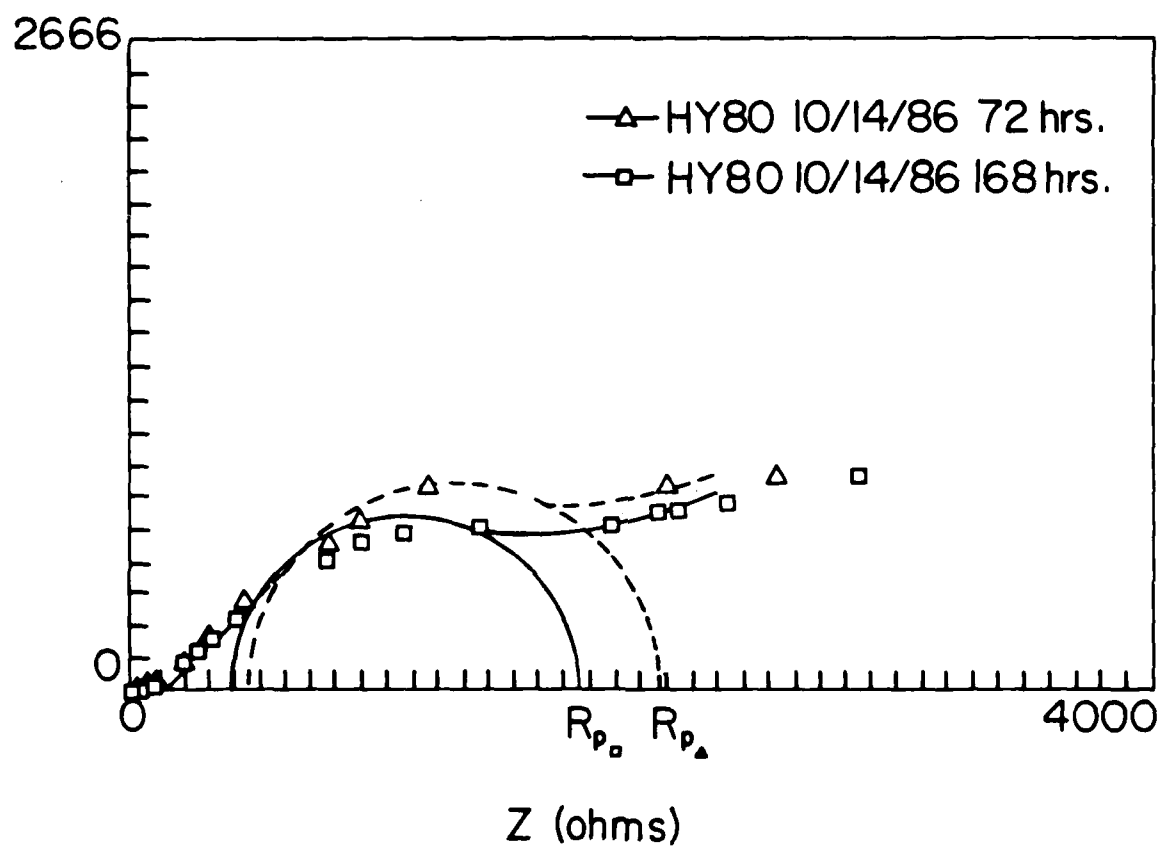


Figure 29 Nyquist plot for HY80 Steel in Seawater. Presence of Larger Semi-Circle Due to the Film Impedance Acting as a Diffusion Barrier.

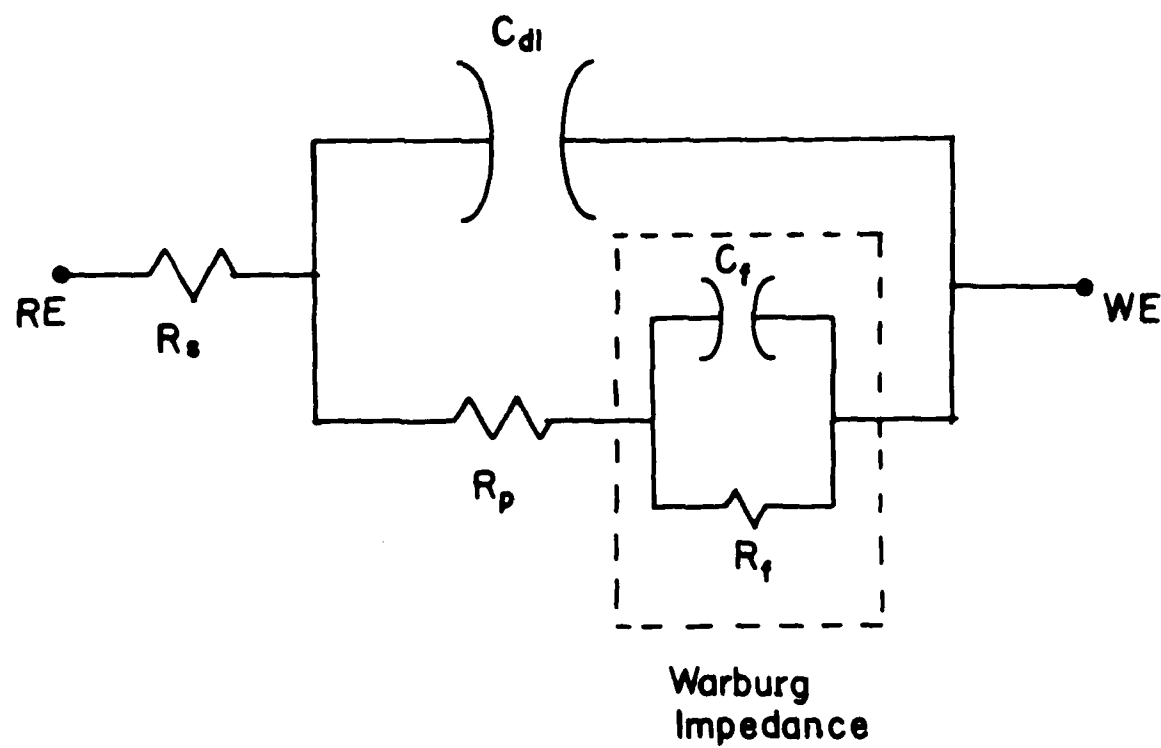


Figure 30 Equivalent electrical circuit of the working cell.

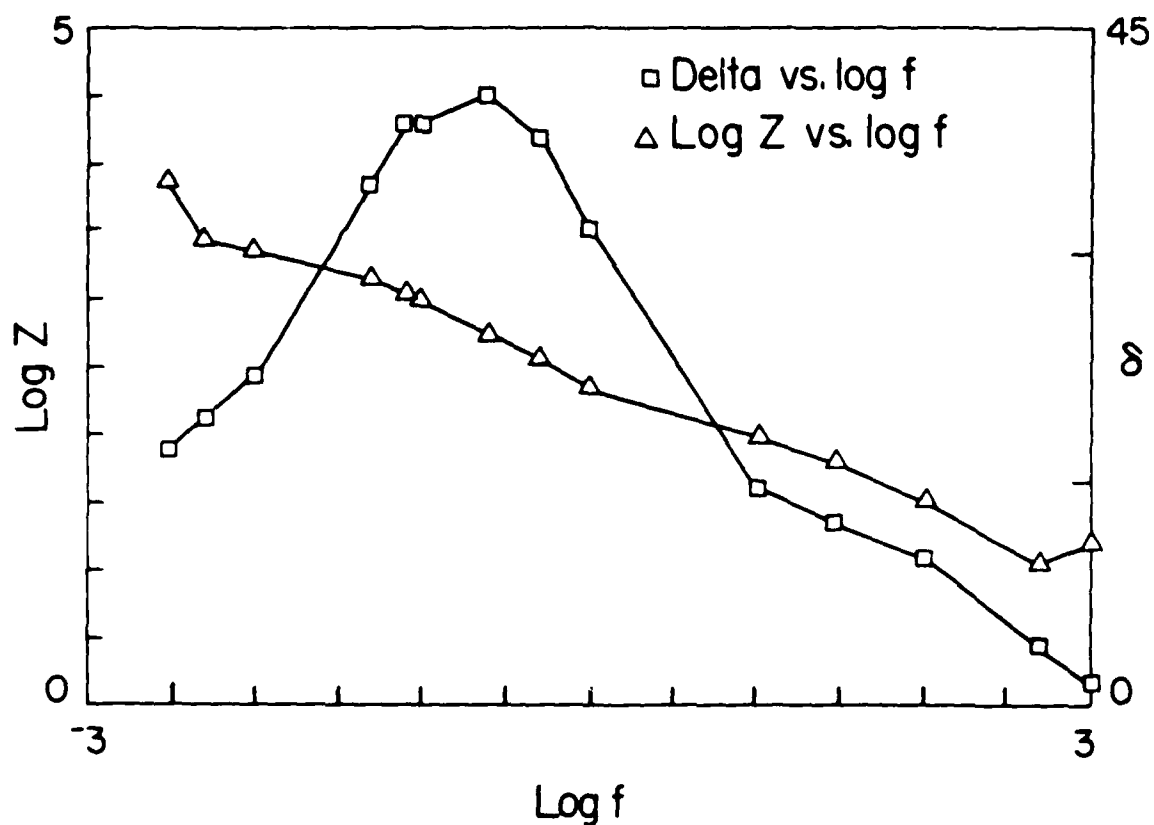


Figure 31 Bode Plot for HY80 Steel in Seawater. Peak in Delta vs. Log f Curve Gives Information on the Smaller Semi-circle from Figure 1.

DC measurements can be used to find the total resistance (R_t) which is given by:

$$R_t = V_{app}/i_{app} \quad (1)$$

where V_{app} is the applied potential, i_{app} is the applied current. R_t is as follows:

$$R_t = R_s + R_p + R_f \quad (2)$$

where R_s is the solution resistance (effectively zero), R_p is the polarization resistance, which can be determined from the Nyquist plot, and R_f is the film resistance which can now be determined. Initial results give typical values of the polarization resistance of 2,000 ohms and film resistances of 20,000 ohms.

Film Adhesion

Several methods of testing adhesion have been considered. Initially a pull tape method was given prime consideration. This method was to consist of bonding cellulose acetate tape to the film and measuring the force needed to pull the tape off. The main disadvantage of this method was that it could not be performed on the film in the wet state. Upon further investigation it was decided that this was a requirement of any adhesion test. The film adherence and strength in situ are critical to resistance to velocity effects and spalling and it is not felt that the values of these properties in the dry state give much indication of how the film would perform wet.

A scratch test similar to the one commonly used in the coatings industry is presently being developed which allows

the determination of film adherence and strength in the wet state.

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